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PROPERTIES OF REACTIVELY SPUTTERED WN$_x$ FILMS

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ABSTRACT

Tungsten nitride (WN$_x$) films were prepared by reactive rf sputtering of a
tungsten target in N$_2$/Ar plasma. The resistivity, intrinsic stress and atomic
composition of the films were studied as functions of various sputtering
parameters: sputtering power, gas pressure, gas composition and substrate
bias. The atomic percentage of nitrogen (x) of the WN$_x$ films was found to
decrease with sputtering power and to increase with the partial pressure of
nitrogen. The intrinsic stress of WN$_x$ is compressive. The dependence of film
properties upon sputtering parameters for WN$_x$ differs significantly from that
of reactively sputtered TiN films, and may be attributed to the difference in
the formation mechanisms of TiN and WN$_x$.

INTRODUCTION

Tungsten nitride (WN$_x$) thin films have been investigated recently as
diffusion barriers in Si and GaAs contact metallizations [1-3], or as high
temperature Schottky gates to GaAs MESFET [4-6]. WN$_x$ can be formed easily and
reproducibly by reactive sputtering from a W target in a nitrogen and argon
gas mixture. Reactively sputtered TiN is the most widely investigated system
[7-9]. Important properties of TiN from the point of view of diffusion
barrier application (resistivity, intrinsic stress, impurity content, etc.)
depend critically on the sputtering conditions.

Despite the fact that WN$_x$ has already been considered for use in device
applications, little is known about the film properties as a function of
deposition parameters. In this study, we report on the influence of various
sputtering process parameters, such as the power, total gas pressure, partial
pressure of nitrogen, and substrate bias on the composition, deposition rate,
resistivity and intrinsic stress of WN$_x$ films.

EXPERIMENTAL PROCEDURE

Silicon wafers, carbon substrates and thin cover glass slides (18 x 18 x
0.160 mm^3) were used as substrates. Prior to loading into the chamber,
silicon wafers and glass slides were processed through cleaning steps in
ultrasonic baths of TCE, acetone and methanol. All WN$_x$ films of this study
were deposited by reactive rf sputtering using a planar magnetron W cathode of
7.5 cm diameter. The substrate holder was placed about 7 cm below the target
and was neither cooled nor heated externally. The sputtering system is
equipped with an oil diffusion pump and a chiller trap that yields a
background pressure about 1×10^{-6} Torr prior to sputter deposition. Prior to
striking the discharge, the total gas pressure of premixed N$_2$/Ar gas
(subsequently referred to as an "initial" gas pressure) was adjusted with a
variable leak valve and monitored with a capacitive manometer. Films were
sputtered with a total gas pressure of 5, 10 and 15 mT. The relative partial
pressure of nitrogen, defined as the ratio of the partial pressure of nitrogen
to the total gas pressure, $p(N_2)/p(N_2+Ar)$, was varied from 0% to 70%.

A Sloan Dektac stylus instrument was used to measure the thickness of the
films. Their resistivities were then determined from sheet resistance

measurements with a four-point probe. The atomic composition of the films was determined by backscattering spectrometry. Carbon substrates were used for these measurements to increase the accuracy of the nitrogen/tungsten ratio derived from the backscattering spectrum.

The film stress was determined using the Dektac stylus instrument by measuring the resulting deflection profiles of the thin cover glass samples. Original deflections of the glass substrates were taken into account. Details on the procedure are given in reference [9].

RESULTS AND DISCUSSION

The crystallographic structure of sputter-deposited WN_x depends on the concentration of nitrogen [10] in films. At low nitrogen concentration (below ~ 15at.%), the films contain a mixture of αW (BCC) and βW (cubic; A15). An amorphous phase is observed in the range of $\sim 15 \div 30\%$ nitrogen. Above that, a single fcc W_2N phase is shown by x-ray but with an increased lattice constant up to 4.28A (bulk 4.126A).

Fig. 1 shows the dependence of the nitrogen concentration of the WN_x films on the dissipated sputtering power for 3 different initial total gas pressures: 5mT, 10mT and 15mT. The percentage of nitrogen in the admitted sputtering gas is kept at a constant level of 40% for each deposition. The nitrogen concentration decreases continuously as the sputtering power is varied from 100 to 600W. There is no sharp transition in the nitrogen concentration of the deposited WN_x films as power changes, although x increases more rapidly below 300W for the case of 10 and 15mT. Sputtering power clearly has a strong influence on the stoichiometry of the WN_x. For 10mT initial total gas pressure, the nitrogen level in the films can be changed 10 fold (from 5% to 50%) by varying the power from 100W to 600W.

Another important feature that is immediately noticable is that increased nitrogen levels can be incorporated in the films when the initial total gas pressure rises. This effect of initial total gas pressure on the composition of the film is most pronounced at 600W sputtering power. For 5 and 10mT gas pressure, the nitrogen level in the films are almost below the detection limit of backscattering spectrometry (BS). However, with 15mT, more than 20 percent of nitrogen is present in the films. This observation contrasts that of the TiN case in which the N/Ti ratio changes negligibly over a wide range of initial total gas pressure [7]. On the other hand, changing the initial total gas pressure influences the deposition rate of the WN_x films insignificantly (Fig. 1). For all three gas pressures, the deposition rate increases almost linearly with sputtering power with the same slope.

Figure 2 shows the dependence of the nitrogen concentration in the WN_x film on the relative nitrogen partial pressure for an initial constant total gas pressure of 10mT and two sputtering powers as parameter. Increasing the initial nitrogen partial pressure (p_{N2}) increases the nitrogen level in the films for both 200W and 400W sputtering power. This agrees well with previous work [1,10]. Sharp increases in nitrogen concentration are observed when p_{N2} is raised beyond 30%. Such increase appears real, and is reflected in the change of deposition rate in the case of 400W: rapid increase in nitrogen concentration in films as p_{N2} changes is accompanied by relatively rapid decrease in deposition rate. This correlation between nitrogen incorporation and deposition rate is not so obvious in the 200W case. Although the deposition rate of WN_x decreases with the amount of relative nitrogen partial pressure during sputtering, the decrease is not as abrupt as in the case of TiN. In the TiN case, there exists a threshold in the nitrogen initial partial pressure above which TiN can be deposited. Passing through this threshold always results in a very abrupt change of sputtering rate.

Figure 3 shows the resistivities of the WN_x films as a function of film compositions. The resistivity values are taken from all our films deposited under every sputtering conditions discussed in this paper for which the
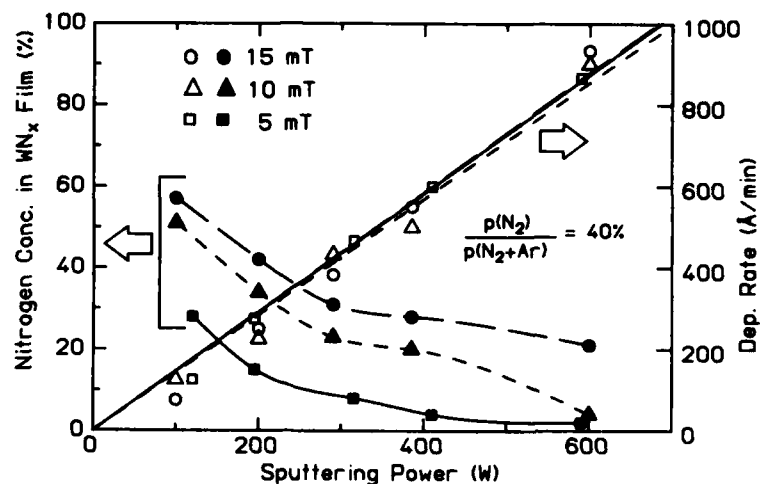
Fig. 1 Nitrogen concentration in the WN$_x$ films and deposition rate for samples sputter-deposited with a fixed 40% N$_2$/60% Ar gas mixture at 5, 10 and 15mT of initial total gas pressure.
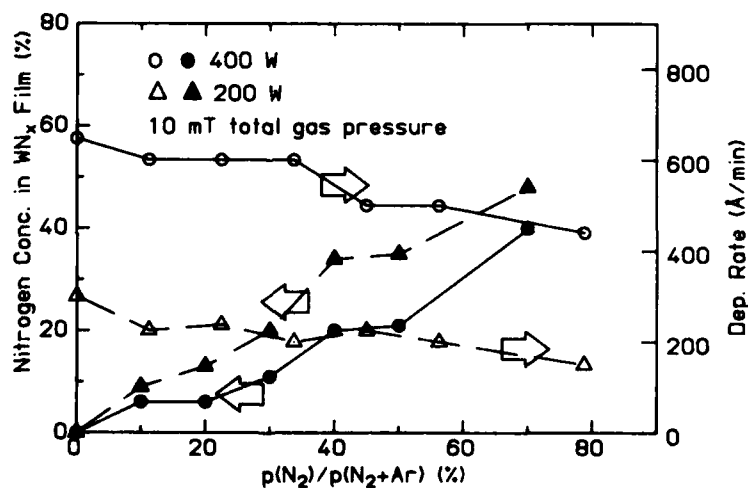

Fig. 2 Nitrogen concentration in the WN$_x$ films and deposition rate as a function of initial relative partial pressure of nitrogen in the gas mixture with a fixed initial total gas pressure of 10mT for samples deposited with 200W and 400W sputtering power.

substrate bias was zero. Some data points were obtained from previous work by Kattelus et al. [1]. It is clear that the resistivity of WN_x increases monotonically with the nitrogen content in the films, regardless of the sputtering parameters. The resistivity rises slowly with nitrogen concentration up to about 30at.% (x < 0.43). Above that, the increase in resistivity steepens. This transition in resistivity also corresponds to the transition from amorphous WN_x to polycrystalline WN_x as x increases. For films containing about 50% nitrogen, resistivities are in the range of 2000 $\mu\Omega$cm (not plotted in Fig. 3). All the amorphous WN_x films have resistivities in the range of $\sim$200 $\mu\Omega$ cm. The fact that the resistivity correlates with the nitrogen concentration regardless of the sputtering conditions used suggests that the microstructure of the WN_x films is dictated principally by the amount of nitrogen present in the film. Such a correlation is in marked contrast with what was observed for TiN [7-9]. Near-stoichiometric TiN obtained under different sputtering conditions have resistivities that can vary by an order of magnitude. The above observation seems to indicate that the formation mechanism of TiN and WN_x may be quite different.

The stress of all W and WN films is compressive. The variation in stress level with composition of the films is shown in Figure 4. As for the · resistivity, stress is more a function of the nitrogen content of the films than of the sputtering conditions. As the nitrogen concentration increases, the compression of films decreases and reaches its lowest value for amorphous samples near 15 ÷ 20at.% nitrogen concentration. Past this point, stress rises again. Beyond about 30at.% nitrogen, the films are polycrystalline and consist of the W_2N phase. According to previous work [10], increasing the nitrogen concentration in W_2N increases the lattice constant from the bulk value of 4.126A to 4.28A at about 45at.% of N. This fact suggests that the excess nitrogen atoms are incorporated into W_2N lattice and that the increase of compressive stress originates from lattice expansion. In this respect, W_2N is similar to TiN [7,8].

Figure 5 depicts the change in composition, resistivity and compressive stress for two WN_x deposition conditions at a fixed initial total pressure of 15mT (25% nitrogen partial pressure, 400W dissipated power, and 40% nitrogen partial pressure, 200W dissipated power) versus negative substrate bias. With an increase in the negative bias the concentration of nitrogen in the films and their resistivities decrease. This result is in good agreement with the fact that resistivity is determined mainly by concentration of nitrogen in the films (Figure 3). In terms of internal stress, the two samples show opposite dependence on negative substrate bias. For the film with low nitrogen concentration, the compression rises as the negative bias increases; for the film with high nitrogen concentration, the trend is opposite. This outcome is as expected from Fig. 4. This response to a negative substrate bias differs radically from that observed for TiN films [8,9]. There, an abrupt transition is observed in the internal stress, the resistivity and the film color in a very narrow range of negative bias values (10V).

CONCLUSIONS

We believe that the results presented here are indicative of reactive sputtering mechanisms for WN_x that are different from those of TiN. The following facts argue for such an interpretation:

(i) When the rf power is increased, all other parameters being fixed, the nitrogen content in the WN_x film decreases monotonically and can approach zero (i.e. pure W is deposited) without short discontinuity in the deposition rate. That is not so for TiN.

(ii) The deposition rate of WN_x depends primarily on the dissipated power, and little on total gas pressure and composition. For TiN, large changes in deposition rate are noted with changes in the total pressure and gas composition at fixed power.
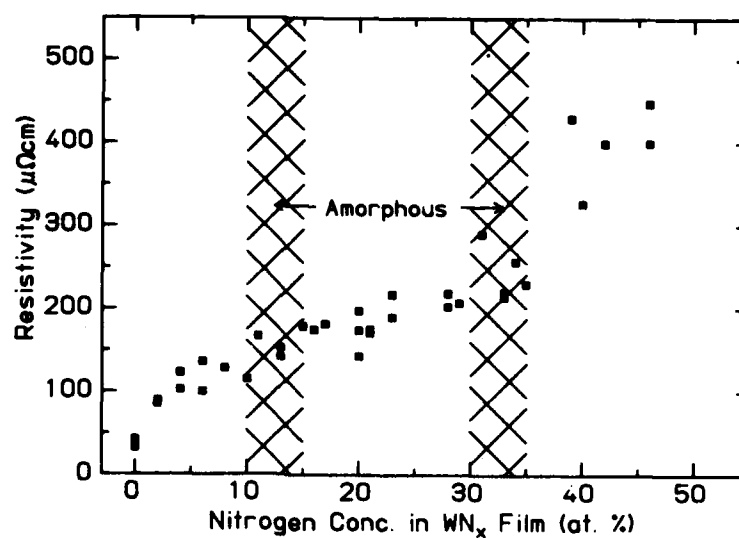
Fig. 3 Resistivity of WN$_x$ films as a function of their nitrogen concentration. The data include all our films deposited under all different sputtering conditions.
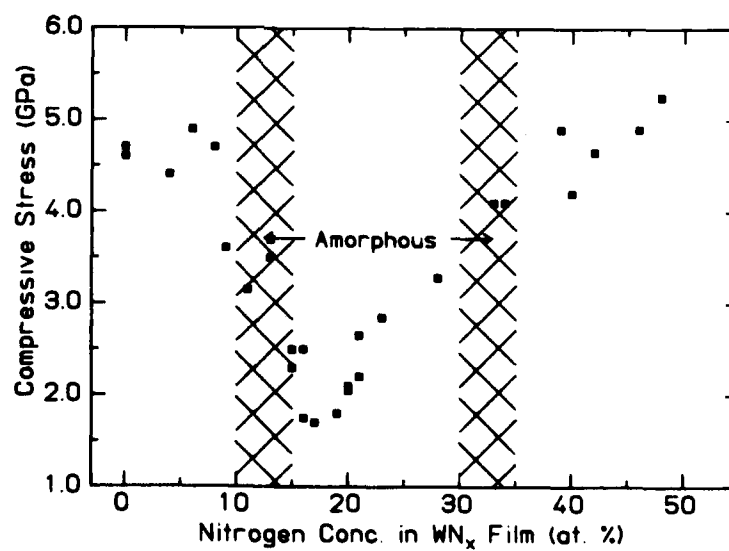

Fig. 4 Compressive stress of WN$_x$ films as a function of their nitrogen concentration. The data include all our films deposited under all different sputtering conditions.
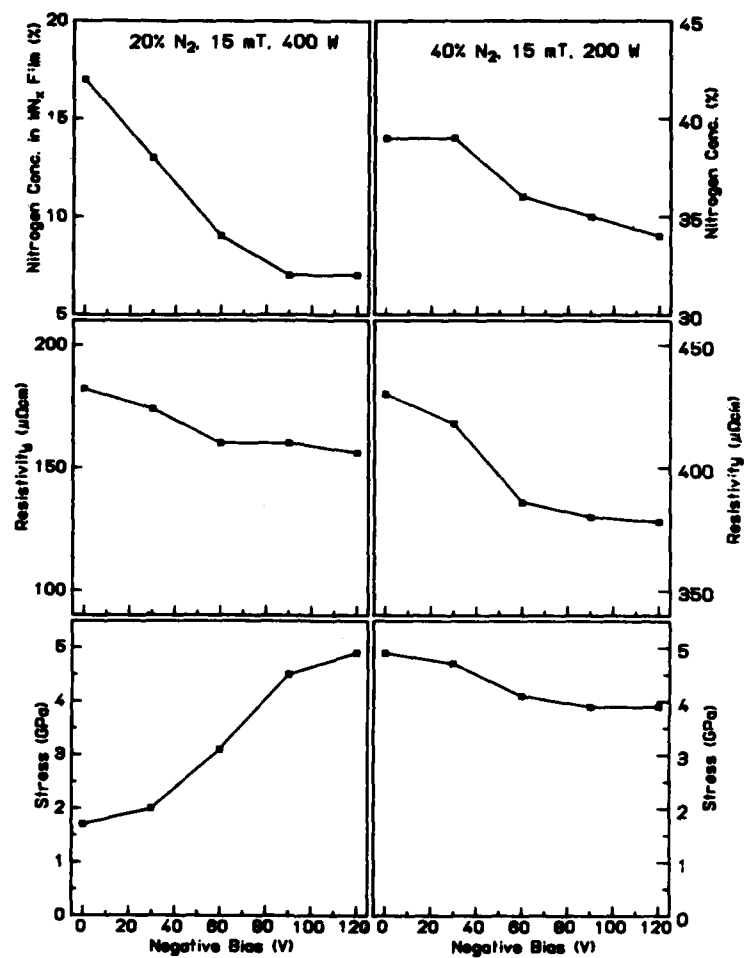
Fig. 5 Influence of a negative substrate bias on the composition, resistivity, and compressive stress of WN$_x$ films deposited under two sputtering conditions for a fixed initial total pressure of 15mT: 25% relative nitrogen partial pressure and 400W of power dissipated at the target, and 40% relative nitrogen partial pressure and 200W of power dissipated at the target.

(iii) A negative dc bias of the substrate changes the resistivity of WN_x little; for TiN, this bias is critical. The same thing is true for the compressive stress.

The reactive sputtering characteristics of WN_x are attractive for industrial application because of the monotonic dependence of the film parameters on the sputtering conditions.

ACKNOWLEDGEMENTS

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